Chapter

Azoles for Renewable Energy Development and Wood Treatment

Nana Derkyi

Abstract

Azole applications in energy are empirical and, despite increasing interest in azole and energy research, many challenges remain in synthesizing and processing azoles with functionality for energy applications. The use of azole in wood treatment has been effective to some extent in producing durable wood; however, there is still the need for improving the treatment of wood species. This chapter seeks solutions which are developed systematically with scientific validation principles. Consequently, this chapter aims to provide a concise overview of integrating azoles in materials used for renewable energy processing and applications, and wood treatment, with an outlook on challenges and opportunities.

Keywords: azole applications, organic solar cells, polymer electrolyte membranes, fungal decay, wood treatment, functionality, copper azole, overview

1. Introduction

There exists a huge demand for favorable new materials in the research space. With this huge demand, the building of a wide array of custom-made materials for different and also multiple applications have been made possible. Most often, the design of conjugated molecules is commonly built around small functionalized aromatic polycyclic systems like azole (**Figure 1**). These systems are built up as pieces of larger conjugated systems like polymers.

In an energy setting that progressively requires efficient and cleaner energy sources, fuel cells are considered as promising electrochemical devices for meeting such demand. This is because they can deliver electric energy with high efficiency and low environmental effect, converting the energy kept in fuels with no pollution. The proton-exchange membrane fuel cells (PEMFC) are known to be one of the most promising sources within the numerous kinds of current fuel cells owing to their great power density and high power-to-weight ratio. One of the downsides of current cells is linked to the electrolytes presently in use, which limit their use to temperatures below 100°C when working with water-assisted proton conduction [1–4]. Operating temperatures above 100°C increase the performance of PEMFC due to a quicker electrode reaction which takes place without carbon monoxide poisoning of the platinum electro-catalyst, high energy efficiency and easier heating, [1–4]. Organic semiconductors (OSCs) have attracted much attention over the past few decades owing to their unique properties, which allow them to be included in a host of electronic device applications.

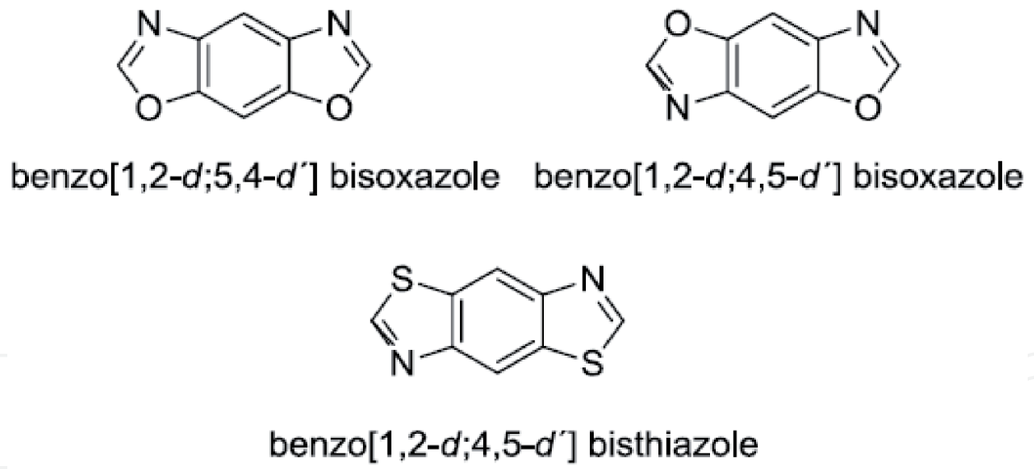

Figure 1.
Basic benzobisazole units.

Wood has been used as a traditional material for the construction of marine structures, such as groynes and jetties [5], and yachts and other boats. The application of wood in marine structures is attributable to the wood explicit properties. The factors for utilizing wood in marine structures include ease of construction and repair, relatively low energy costs of production, high strength-to-weight ratio, and renewability. However, biodegradation of wood is predominantly harsh in maritime construction due to the action of marine wood borers and crustaceans, in contrast to beetles, decay fungi, and termites active above the waterline [6]. In borer attack prevention, biocides are, in some cases, used to treat wood [6].

The use of durable hardwood species, mostly tropical hardwoods which are resistant to biodegradation, has led to tropical deforestation that continues to be a cause of concern. There are many other factors associated with this tropical deforestation other than the use of timber in maritime structures. The decrease in naturally durable species has necessitated the treatment of softwoods by using preservatives to achieve suitable protection for the wood under service conditions, mainly for outdoor applications [7].

This chapter seeks solutions which are developed systematically with scientific validation principles. Consequently, this chapter aims to provide a concise overview of integrating azoles in materials used for renewable energy processing and wood treatment, with an outlook on challenges and opportunities.

2. Chemistry of azoles

Azole compounds are part of a large class of heterocyclic compounds in Organic chemistry. Azoles are five-membered heterocyclic compounds containing a nitrogen atom and at least one other non-carbon atom of either nitrogen, sulfur, or oxygen [8]. They include the heterocyclic rings in **Figure 2**.

The chemistry of 1,2,3-triazoles gained much attention since the discovery of the copper-catalyzed alkyne-azide cycloaddition (CuAAC) reaction, which delivers the 1,4-regioisomer exclusively in high yields [8].

Triazoles are five-membered aromatic heterocyclics, containing three nitrogen atoms. These atoms may be found arranged consecutively or not, given the isomers 1,2,3-triazoles or 1,2,4-triazoles, respectively (**Figure 3**) [8].

The structure of 1,2,3-triazoles, as shown in **Figure 3**, may exist in two diverse tautomers, per their position of the N-H bond on the ring. The position of the N-H

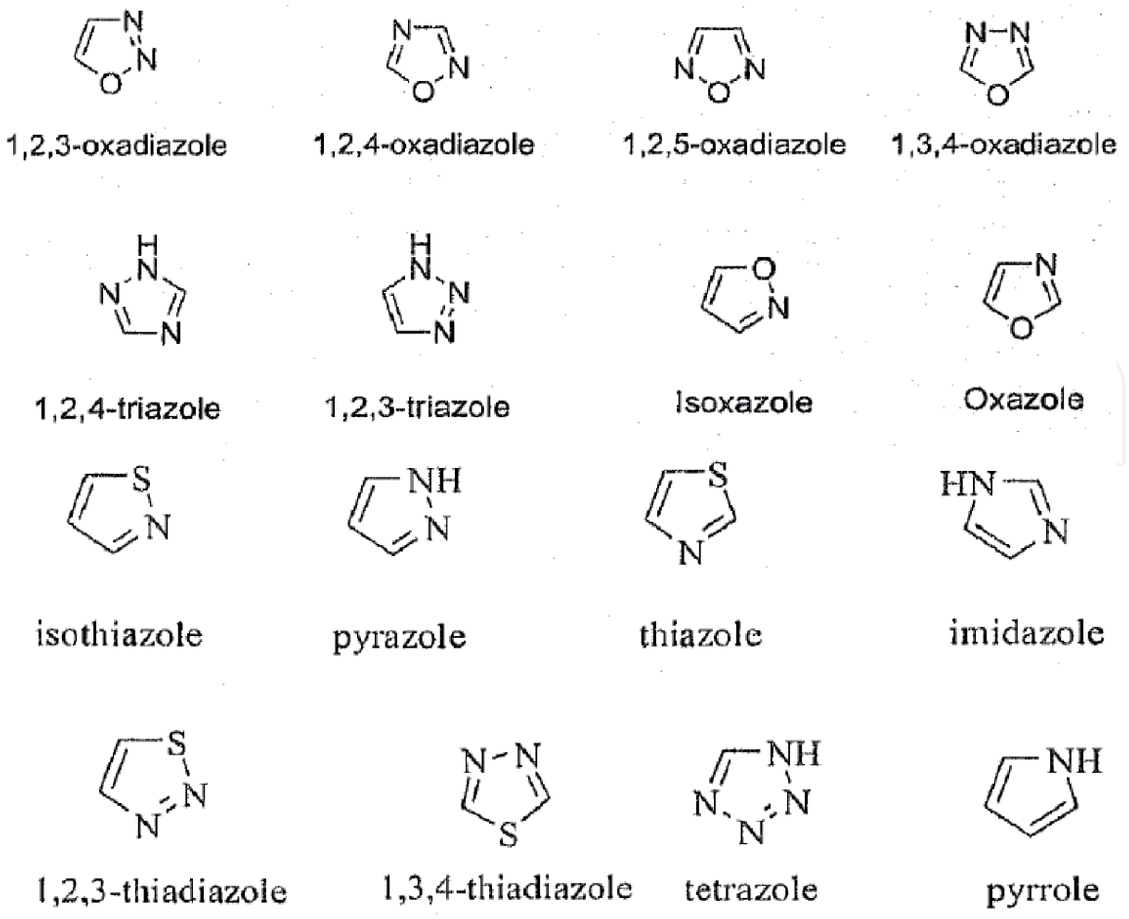

Figure 2.
Examples of azole compounds.

Figure 3.
Structures of isomeric triazoles.

bond can be on nitrogen 1 (1H) or in nitrogen 2 (2H). If the 1,2,3-triazole skeleton is substituted at the nitrogen and carbon atoms, dissimilar regioisomers may be obtained as shown in **Figure 4**.

When compared to their 1,2,4 isomers, the 1,2,3-triazoles have very distinct properties and more importantly, the N2 substituted has different properties than the N1 as well as N3, despite the structural likeness. For instance, the differences in basicity between the N1 and N2 isomers could be responsible for their different behavior within biological systems [8]. The N2-1,2,3-triazole core is found in several bioactive compounds, including antifungals [8]. The different tautomers shown in **Figure 5** have distinct physical, chemical and biological properties [8].

The substitution of the triazole implies the study of the N3 -H tautomer, in addition to the N1 -H and N2 -H. **Table 1** gives a summary of some energy values obtained by substituting the 1,2,3-triazole at carbon with different substituents, generating tautomers. It has been observed that in all cases studied, the N2 -H tautomer is the most stable. **Figure 6** depicts substituent X on the different

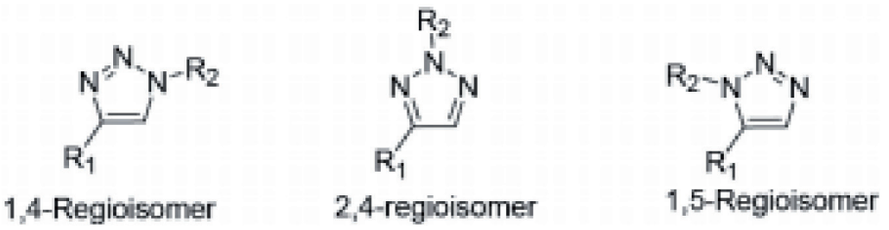

Figure 4.
Substituted 1,2,3-triazoles with dissimilar regioisomers of carbon and nitrogen.

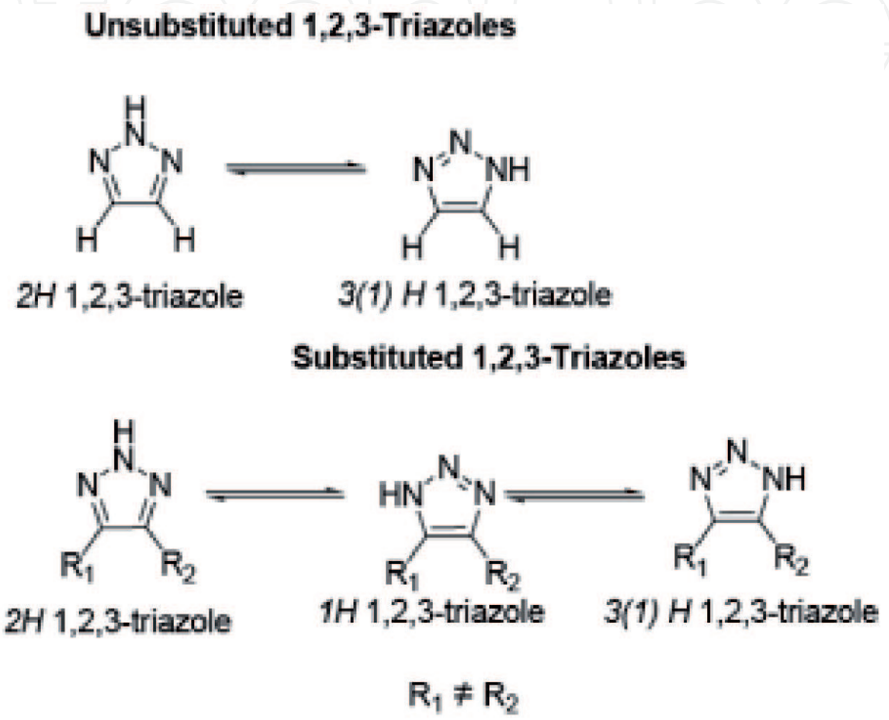

Figure 5.
Different tautomers of substituted and unsubstituted 1,2,3-triazoles [8].

X	ΔE (kJ/mol)		
	N^3	N^2	N^1
NH_2	30.734	0	22.019
F	37.059	0	21.340
Cl	27,557	0	20,780
CH_3	20,566	0	20,080
CN	22,475	0	18,004
NO_2	22,194	0	16,941
CHO	17,188	0	15,530
COOH	12,081	0	13,261
OH	35.946	0	18,578
$CONH_2$	23,266	0	10,892
BF_2	12,336	0	16,966
BH_2	5547	0	15,815

Table 1.
The relative energy of N1-H and N3-H to N2-H in the presence of different substituents [9].

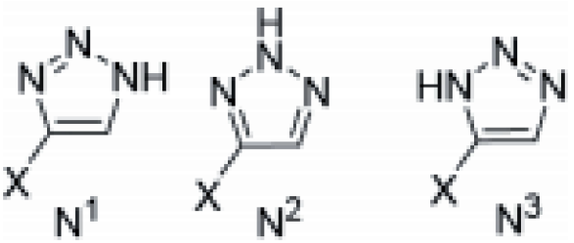

Figure 6.
Substituents on different azole tautomers.

tautomers, and from **Table 1** it can be realized that the substituent X has a strong correlation on the stabilization of the N1-H tautomer against the N3-H tautomer. It can be observed from **Table 1** that the donor or electron-withdrawing performance of different groups does not render differences in the stabilization of the tautomers. However, the steric hindrance and hydrogen bonds between the substituent and the adjacent azole nitrogen atom which seem to be the preeminent factor in the stabilization of N1-H versus N3-H.

Azoles are known for their broad-spectrum biological activities including antimicrobial, anti-inflammatory, analgesic, antimitotic, anticonvulsive, diuretic and many other uses as main ingredients in many drugs, [10]. Azoles are also known for their usage wood preservatives [11].

Generally, isolated natural products of heterocyclic nature act as lead compounds for the development of new molecules of bioactive interest. Also, most of the heterocyclic compounds are synthesized from readily available fine chemicals. In this respect, synthesis and characterization of new molecular entities incorporating heterocyclic structures are of great importance.

Azoles constitute a crucial category of antifungal agents in clinical, agricultural, and wood treatment uses. In general, they target the inhibition of ergosterol synthesis. Fungi are eukaryotes just like mammalian cells, and so agents that affect protein or nucleic acid biosynthesis are likely to display general eukaryotic toxicity [12]. Ergosterol, the predominant component of fungal cell membranes, is, therefore, evident and specific target for fungal inhibition.

3. History of azoles

In the beginning of the development of organic chemistry, heterocyclic chemistry of which azoles belong has held center stage in the development of molecules to enhance the quality of human life. Examples include drugs development, agricultural produce and wood preservation, as well as energy applications [8, 13]. Some of these organic compounds, as early as the 1950s, had been reported to have electrical conductivity [13]. However, the first breakthroughs did not occur until the 1970s. OSCs have been incorporated into various electronic devices, including organic photovoltaics (OPVs) [14, 15], some of which have been developed commercially [16, 17].

Researchers had become interested in the antifungal activity of azole compounds since 1958 after the introduction of topical chlormidazole. However, the first report of the antifungal activity of an azole compound, benzimidazole, was already described in 1944 by Woolley [18]. The initial reports of antifungal properties for imidazoles were published in the late 1960s [19]. During that period, three new topical compounds: clotrimazole, developed by Bayer Ag (Germany), and miconazole and econazole, both developed by Janssen Pharmaceutica (Belgium) were introduced [20].

There have been significant changes in the wood preservation industry over the past several years. For ground contact applications, copper-based systems have replaced the chromate copper arsenate (CCA) product used for many years but had some corrosion and mold issues during the initial phases of the transition [20]. Creosote was virtually the only preservative until various new preservatives were introduced in the 1930 and 1940s. There was a continued evolution of preservative systems, and in 1990, copper-azole preservatives were introduced [20].

4. Azole-based materials for renewable energy applications

There is quite a large number of azole compounds that are suitable for energy applications. These include but not limited to imidazoles, diazoles, triazoles, tetrazoles, thyazoles and pyrazoles [2]. A fuel cell, which is a device that provides electrical energy with high efficiency and low environmental impact, converts the chemical energy stored in fuel, such as hydrogen, methanol, ethanol, etc., directly and efficiently to electrical energy. In fuel cell applications, the fuel cell consists of thermal, humidification, and reactant/product management systems, electronics, and the membrane electrode assembly (MEA) [2]. The membrane electrode assembly is the electrochemically active portion of the cell, which contains an ion-permeable but electrically non-conductive electrolyte sandwiched between an anode and cathode at which oxidation of fuel and reduction of oxygen occur. Organic ionic liquids, molten salts, and strong acids/bases can all be utilized as the electrolyte separating anode and cathode. However, to minimize corrosion and gas diffusion and to improve the mechanical strength of fuel cells, solid oxide and polymer electrolyte membranes are the predominant separators in modern systems. Engineering of the complete fuel cell, including its support systems, is, therefore, an essential task in which the materials and chemistry are focused on the electroactive MEA. Thus, the proton-exchange membrane (PEM) is a significant component for the operation of proton-exchange membrane fuel cell (PEMFC).

Generally, PEM are made of polymeric organic compounds containing acidic functions (example, Nafion). The restrictions of modern membranes have nurtured the research and development of alternative membranes, including doped polybenzimidazole (a combination of Nafion and metal oxides), organosiloxane based on inorganic-organic hybrids with various acidic species, and sulfonated polymers based on aromatic hydrocarbons [8–14].

Typically, some amount of hydration is essential to conduct ions, and there are some new materials merging acceptor and donor ion carrier abilities of numerous groups [10]. Heterocyclics do act as a proton-conducting species, due to the amphoteric behavior of nitrogen. Thus, they can be used either as dopant or pendant groups in PEMFC devoid of the need to use external humidification. The properties of numerous heterocyclics, including benzimidazole and triazole, permit them to be used in materials operational above 100°C [21–24].

Several azole derivatives have been synthesized to become precursors for novel fuel cell membrane materials. For example, from the azole compound 4,7-dibromobenzimidazole, new phosphonate-, hydroxybisphosphonate- and aminobisphosphonate benzimidazole derivatives substituted at N-1 position have been synthesized in good yields. Again, new regioisomers of phosphonate- and aminobisphosphonatebenzotriazole derivatives substituted at N-1 or N-2 positions have been synthesized in good yields from 4,7-dibromobenzotriazole. Characterization by NMR, IR spectroscopy and mass spectrometry (low and high resolution) of these compounds have been fully done allowing the assignment of regioisomers [24].

Considering chemical viewpoint, two principal structural features give rise to the properties of organic semiconductors (OSCs). These are conjugated core or support, and countless types of solubilizing side chains. These two structural features, exact by chemical synthesis, have a wide influence on the nano-scale morphology, optoelectronic energy levels, and the bulk physical features of these materials.

Standard monomer building blocks to construct conjugated polymer for solar cells include azoles, and they are categorized by the number of rings and way of linking. Polybenzobisazoles, a class of polymers that are known for their exceptional thermal stability and high tensile strength of fibers spun from them, are important in organic solar cells applications. 9 An example is poly(*p*-phenylene-2,6-benzobisoxazole) which is a liquid crystalline polymer based on benzo[1,2-*d*; 4,5-*d*']benzobisoxazole that is spun into fibers commercially sold under the name Zylon® [25]. Because of the previous use of polybenzobisazoles in high-performance applications, all of the necessary monomers can be synthesized on an industrial scale, and purified without the use of column chromatography. This ability to synthesize monomers on an industrial scale is advantageous for large-scale synthesis. Furthermore, the benzobisazole ring system is electron-deficient and planar, which leads to strong intermolecular interactions and good charge transport properties within polymer films [26].

5. Current trends and prospects of azoles in renewable energy development

5.1 Fuel cells

The quest for clean and efficient energy has motivated the search for new materials to develop environmentally friendly energy applications. Fuel cells have potential for alternative clean and efficient energy conversion devices with zero pollution [1, 27]. Considering the various kinds of fuel cells, the proton-exchange membrane fuel cells (PEMFCs) are known to be sources of power, due to their inherent great high power-to-weight ratio and power density. The PEM is a key material for the operation of PEMFC. In recent years, PEM has been a focus of many research works, to obtain membranes with good chemical/thermal stability, high proton conductivity, low electrical conductivity, low permeability to fuel and oxidant, good mechanical properties and cost-effective [1, 27]. Temperature is a critical factor in operating PEMFCs due to its correlation with the water content of fuel cell. The processes above 100°C increase the performance of the fuel cell due to quicker electrode reaction without carbon monoxide poisoning of the platinum electrocatalyst, easier heating, water consumption management and high energy efficiency [1, 27]. The PEM is usually made of polymeric organic compounds containing acidic ends; however, the proton transport properties of these membranes are strongly related to the water content and, therefore, limit their operating temperatures up to 90°C [1, 27].

The limitations of temperature have brought about an increased interest in research and development of new alternative membranes. Among them, a variety of membranes have been developed as alternative to the perfluorosulphonic polymers,, such as polybenzimidazole (PBI)-doped composites of Nafion and metal oxides, sulfonated polymers based on aromatic hydrocarbons, and organosiloxane polymers based on inorganic-organic hybrids with various acidic species [1, 27].

Azoles as amphoteric species conduct protons as pure compounds. Recent computational studies are geared towards elucidating the mechanism underlying structural diffusion in some of these amphoteric species. In protonated imidazole, charge

transport occurs via a method directly analogous to aqueous transport, exhibiting rapid molecular reorientations and a shifting hydrogen bond network [28].

In several azole-based systems, proton conductivity is being investigated by pulsed field gradient spin-echo nuclear magnetic resonance (PFGSE-NMR) and impedance spectroscopies, to confirm results obtained by computational simulations [29, 30]. Improving the proton conductivity of polymer electrolytes under high temperature and low humidity conditions by imbibing polymers (**Figure 7**) that exhibit favorable hydrated properties with small-molecule amphoteric species is a current research agenda. These molecules effectively replace the water that would traditionally exist as a proton solvent, enabling proton conduction under these dehydrating conditions. Doping studies of PEM with azoles are thus high on the research agenda [31, 32].

5.2 Solar cells

Enormous potential exists in solar energy to take the place of fossil fuels due to its vast energy stock and availability worldwide [33]. Solar energy conversion system is traditionally based on silicon technology. However, the wide use of silicon-based solar cell technology is limited by its high power conversion cost [34]. To address this issue, organic solar cell has been developed to replace Si-solar cell [35].

The optoelectronic properties of polymeric semiconductor materials can be used for the fabrication of photonic devices. If key structural requirements are met, these materials exhibit distinctive properties such as solution processability, large charge-transporting capabilities, and/or broad optical absorption. Developments in the area of π-conjugated polymeric semiconductors for bulk-heterojunction photovoltaic cell (BHJ-OPV) or organic solar cell (OSC) applications have been made, and these conjugated polymers (CPs) have become pervasive in photovoltaic cells applications [36].

Conjugated polymers offer several advantages over their inorganic counterparts, including solution processability to reduce fabrication costs, and the ability to tune their properties via organic synthesis, which enables optimization for use in specific applications. Currently, a good and effective strategy for adjusting the optical and electronic properties of conjugated polymers is through the integration of alternating electron-donating and electron-accepting comonomers within the polymer backbone. This approach which is a current trend, has afforded many materials with narrow bandgaps suitable for effective harvesting of solar energy. For example, a synthesis of benzo[1,2-c:4,5-c]bis[1,2,5]thiadiazole containing donor-acceptor monomers and their acid-catalyzed polymerization has been reported [37].

Conjugated polymer-based solar cell (PSC) has several important advantages compared with conventional Si-based solar cell. These include solution processability by spin-coating, ink-jet printing and roll-to-roll processing to reduce manufacturing cost; tunable physical properties, and mechanical flexibility for PSC application on curved surfaces [38].

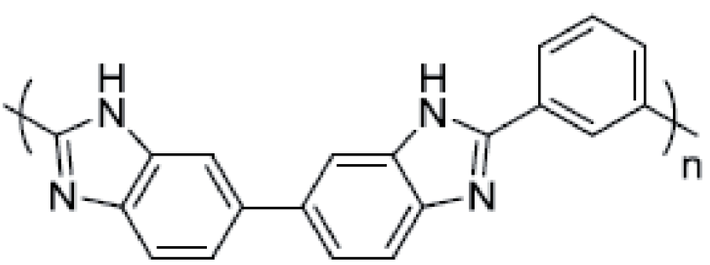

Figure 7.
Chemical structure of unsubstituted polybenzimidazole (PBI) (poly-2,2-m-phenylene-5,5-bibenzimidazole).

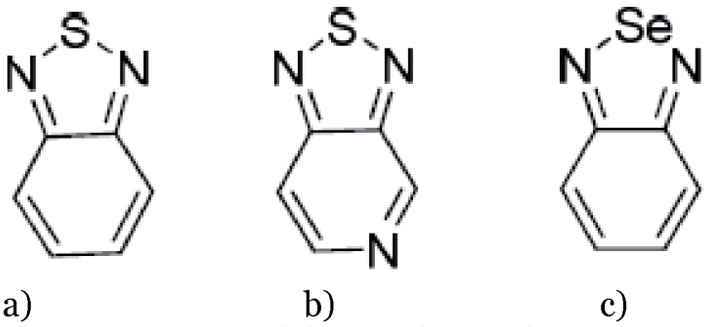

Figure 8.
Structure of (a) BT, (b) aza-BT and (c) Se-BT.

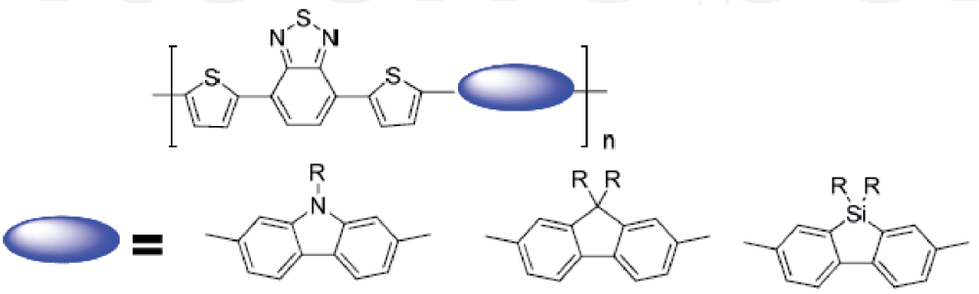

Figure 9.
Benzothiadiazole containing low bandgap polymers.

An important electron-accepting unit in organic electronics including organic solar cells is 2,1,3-benzothiadiazole (BT). Two types of BT-fused units have been synthesized. These are thiazole-fused BT containing electron-withdrawing C=N bond and imidazole-fused BT containing electron-donating nitrogen atom as well as an electron-withdrawing C=N bond. Theoretical calculations and measurements by electrochemical means suggest that thiazole-fusion enhances electron-accepting ability [39]. In contrast, imidazole-fusion bestows the benzothiadiazole skeleton with electron-donating capacity while sustaining its electron-accepting ability. Besides, in thiazole-fused BT units, the electronic configuration could be additionally controlled by tuning the oxidation number of the sulfur atom in methylthio group at the fused thiazole ring [39]. Thus, the electron withdrawing ability of BT can be further increased by replacing one carbon atom with sp^2-hybridized N atom (**Figure 8**).

A variety of low bandgap polymers containing BT have been synthesized and tested for PSC performance (**Figure 9**) [40, 41].

6. Challenges of azoles in renewable energy development

Doping of azoles with strong acids can bring about the problems, including incorporating some of the undesirable anhydrous properties of these acids (e.g. high water uptake, physical stiffening of the polymer matrix) into mixed materials. In fuel cells applications, introducing polymer electrolytes with small-molecule proton solvent does not entirely solve the problem of anhydrous proton conductivity. For instance, imidazole still evaporates or is washed from the membrane over time. Also, unlike water, its equilibrium partial pressure in the surrounding atmosphere is negligible, and once it leaves the membrane, it is not easy to re-introduce. Even for species large enough to have little vapor pressure like imidazoles with long tethers (**Figure 10**), leaking along with the water that is formed and expelled during fuel

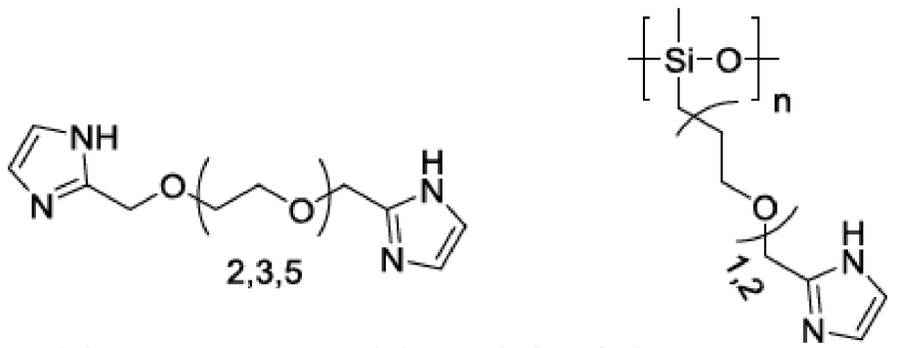

Figure 10.
Tethered imidazoles used to investigate relative rates of a vehicle and structural diffusion in imidazole-based molecules [42].

cell operation is a significant challenge. This leaking leads to both loss of conductivity with time and potentially to the corrosion of other parts of the fuel cell.

Although some recent examples of anhydrous proton conducting polymers utilize members of the azole family as proton solvents. Yet, still, comparatively few azoles have been studied to date due in part to the synthetic limitations of available techniques. Also, there is a problem of leaking and other forms of solvent loss which could, however, be overcome by tethering the solvent providing proton transport (e.g. imidazole, phosphoric acid) directly to a polymer backbone. An outcome is that the connectivity and percolation of solvating species is key for conduction in materials where their long-range diffusion is restricted. The low anhydrous conductivities of poly(styrenesulfonic acid) and poly(vinylphosphonic acid) for example, illustrate this effect. **Figure 10** shows azole-based materials with a polymer-bound proton solvent that exhibit measurable proton conductivity [42].

Organic photovoltaic (OPV) systems, in particular, polymer solar cells, made by solution-processed organic materials, have shown great promise as a technology for affordable electricity. Until recently, the commercialization of OPV has been hampered by the difficulty of converting laboratory-produced cell into reliable industrial-scale product performances. Unfortunately, a significant barrier to the introduction of organics into these areas has to do with inferior electrical properties as compared to traditional inorganic semiconductors.

The significant concerns by using some azole polymers arise from the azole synthesis and processing conditions. These azole polymers require very high temperatures (more than 200°C) in highly acidic media (poly(phosphoric acid)) to be synthesized and maintain its solubility after cooling [43]. Molding these polymeric materials into films also necessitates that the materials are dissolved in highly acidic media (conc. Sulfuric acid, aluminum chloride in nitromethane) [43]. Once formed, it is also challenging to get rid of trace acid, which leads to unintentional doping. The performance of organic electronic devices is hampered by the presence of acidic impurities by the interference with charge and exciton transport.

7. Opportunities for utilizing azoles in energy development

Fuel cells, as zero pollution systems have the potential to become alternative clean and efficient energy conversion systems [1]. From previous experiences of utilizing polybenzobisazoles in high-performance applications, all of the necessary monomers for fuel cells can now be synthesized on an industrial scale, and purification effected without the use of column chromatography. This is beneficial for large-scale synthesis of azoles. Furthermore, the ring system of benzobisazole

is electron-deficient and planar, and as a consequence, leads to resilient intermolecular interactions and good charge transport properties within polymer films [44]. The key to conductivity in systems where the proton solvent is tethered to a backbone is rotational and translational mobility of the tethered moiety. While imidazole, phosphoric acid, and sulfuric acid all conduct well as mobile small-molecule liquids, the proximity to poly(vinylphosphonic acid) and stiffness of the backbone in the poly(vinylphosphonic acid) significantly limits these acids' ability to form conductive networks. By contrast, the low glass transition temperature (Tg) of the backbone and flexible tether of the imidazole-containing polymer illustrated in **Figure 10** enables proton conductivity in this material.

Azole-containing polymers are particularly attractive as anhydrous proton conductors due to their chemical diversity and comparatively small changes in physical properties in the presence of water. Sulfonic acids form stiff, immobile clusters at low hydration and absorb significant quantities of water from the atmosphere at high humidity. By contrast, less acidic moieties, such as carboxylic acids (e.g. Surlyn®, a copolymer of ethylene and methacrylic acid) hydrate much less strongly, mitigating changes in properties with changing RH [36]. The weak hydrogen bonding observed in imidazole, and by extension, the azoles in general likewise enables polymers containing these moieties to remain fluid under anhydrous conditions. This property plagues the anhydrous behaviour of sulfonated materials.

The goals of OSC technological development are not necessarily to exceed the performance of inorganics. There is a great opportunity in using combinations of the organics and inorganics. OSCs offer new device functionalities (optical transparency, chemical response, lightweight) as well as a way to produce electronic materials at a lower cost [45]. A critical factor in achieving excellent performance is to develop OPV materials (buffer materials, polymer donors, acceptors, electrodes materials and encapsulants) exhibiting the required technical and economic characteristics to be conveniently used in an industrial environment. The improvement in new materials development remains an important area of research despite the fact that CP-based OPVs are rapidly approaching the 10% power conversion efficiency recommended for them to be of commercial importance. Particularly, the advancement of effective donor materials that takes into consideration practical aspects of commercialization such as enhanced environmental and thermal stability of the resulting material, facile synthesis and purification of monomers, is still pertinent. The most attractive part about the use of OSCs instead of using traditional inorganic semiconductors, is derived from the synthetic range intrinsic in organic molecules. There exist many different ways to alter the properties of OSCs by chemical synthesis, making the OSCs easily tunable to fit the needs of a device [46].

Still needed for commercialization of azole-based materials for energy applications is the continued improvements in efficiency, stability, and cost. Ongoing research and development of azole materials, devices, and systems are making significant advances, benefiting from strong synergies with current research efforts in photovoltaics, nanotechnologies, and azole materials. In this vein, efficiencies are being improved through enhanced sunlight absorption and better surface catalysis.

8. Wood preservatives

Wood preservatives are known to be chemicals impregnated into wood to help with the resistance of attack by mold, decay fungi, and termites. When a wood may be in contact with humans or will be painted, waterborne wood preservatives are commonly used in their treatment. Different formulations of waterborne

preservatives have been made, but only a few of these have been used commercially. Most commercial treatments contain copper ions, which give treated wood its characteristic greenish-brown colouration.

Alkaline copper quaternary (ACQ) amine, a wood preservative, is composed of 67% copper oxide and a 33% didecyldimethylammonium chloride or carbonate (a quaternary ammonium compound) [47]. Since its initial commercialization, the quaternary ammonium compound has been produced using a chloride formulation, which was later replaced with a formulation from a carbonate. Several preparations of ACQ have been commercialized, and it can be treated with an amine or ammonia carrier. Copper azole preservatives (denoted as CA-B and CA-C under American Wood Protection Association/AWPA standards) are composed of 96% ammine copper and a 4% azole. In copper azole type B, the azole is entirely composed of tebuconazole. In type C, the azole is a 50/50 mixture of propiconazole and tebuconazole. While copper azole contains a higher percentage of copper than does ACQ, the retention required for aboveground use [47] is lower and, therefore, the total amount of copper in the treated wood is less.

9. Azole-based materials for wood preservation

Tebuconazole had been first identified by Grundlinger and Exner (1990) as an unleachable, light and heat-stable organic biocide that provides protection against copper tolerant fungi" [48]. Kugler et al. reported of tebuconazole and propiconazole as complementing each other in terms of their efficacy against the brown rot basiodiomycete fungi [49]. The test method for assessing the performance against basiodiomycete decay fungi is EN113, and the toxic values for *Coniophoraputeana* is between 0.08–0.13 kg/m^3 active ingredient [48].

Copper azole type B (CA-B) is formulated from tebuconazole (4%) and amine copper (96%). In copper azole type C (CA-C), half of the tebuconazole in copper azole type B is replaced with the azole, propiconazole. Thus, the copper azole type C consists of 2% tebuconazole, 2% propiconazole and 96% amine copper. A previous preparation, copper azole type A (CBA-A) contained boric acid as a main ingredient in addition to the tebuconazole. Although copper azole is an amine formulation, it may also be formulated with an amine-ammonia compound. The ammonia may be added if the copper azole formulation is used to treat refractory wood species.

Through laboratory screening tests and extensive field trials, copper and triazole were identified as the active ingredients which could offer a viable alternative to CCA. For example, the main active ingredients in the commercial preservative TanalithR E are copper carbonate, tebuconazole and propiconazole, [50]. The ratio of actives as presented by Enviros [51] in their treated timber classification report on a percentage weight/weight basis in the preservative was copper carbonate 20%, propiconazole 0.2% and tebuconazole at 0.2%.

Azole molecules and their derivatives are among the organic corrosion inhibitors for copper that are frequently used. In this vein, density functional theory (DFT) calculations have been performed on the adsorption of four azole molecules; imidazole, 1,2,3-triazole, tetrazole, and pentazole on Cu (III) and Al (III) surfaces, and these have been characterized. It was found out that the molecules adsorb in an upright geometry onto the top site of Cu (III) only weakly, via single nitrogen atom. The chemical bonding with two nitrogen atoms to a bridge site becomes slightly preferred in all the molecules except for triazole. Molecular electronic structure is only weakly perturbed when adsorbed, and hybridization between molecular σ orbitals and metal states constitutes the molecule-surface interaction. Yet, the significant contribution to bonding comes from the electrostatic dipole interactions

due to the dipole-dipole moment of azole molecules. Also, the lateral intermolecular repulsion can be significant and very long-ranged. The molecular electronegativity and chemical hardness increase linearly with increasing number of nitrogen atoms in the azole ring. The harder the molecule the more difficult the hybridization with metal states. This explains why with the increasing number of nitrogen atoms in azole ring the molecule-Cu(III) bond strength decreases linearly as: imidazole > 1,2,3–triazole > tetrazole > pentazole [52].

10. Current trends and future prospects of azoles in wood preservation

Wood-degrading organisms, in conditions that support their growth are generally responsible for the deterioration of many commonly-used wood species if exposed. Wood products are therefore, protected by utilizing chemical preservatives for protection against attack by decay fungi, harmful insects, or marine borers. Treating wood materials with preservatives increases their lifespan, which leads to reduced replacement costs and ensures greater resourceful use of forest trees. The extent of wood protection is dependent on the type of chemical preservative used, and the treatment method used. In terms of effectiveness, some of the chemical preservatives are better than others, while some are also more adaptable to specific applications. For long-term effectiveness, chemical preservative, and treatment method for each wood species are needed for adequate penetration and retention [53].

Wood preservatives must meet two broad criteria which include the provision of the desired wood protection in the intended end-use, and doing so without presenting unreasonable risks to people and the environment. For several decades now, copper-based wood preservatives have dominated the industrial preservation of wood for exterior applications [54].

Materials and products from nanotechnology are increasingly being produced and used for the potential they hold to provide great interests to society. As such, although still emerging, nanotechnology has been identified as a key enabling technology. One of its important areas of application is biocide preservatives for wood protection. One prominent example is copper azole, used in wood preservation through impregnations. The use of nanoscale Cu instead of bulk Cu improves the durability of wood against microbial and fungal activity due to mainly decreased viscosity of formulations and increased effective surface area of Cu, enhancing dispersion stability. These properties contribute to easier impregnation and deeper and more homogeneous uptake of reactive biocide into the wood, which allows continuous and effective protection over its lifetime. In these preservatives, copper is the main biocide, and the azole is a co-biocide. These preservatives have gained a significant market importance in the wood industry.

Copper azole which is a water-based preservative and dependent principally on copper solubilized in ethanolamine and an organic trizaole co-biocide, is a recent development. The first copper azole preservative that was developed consisted of 49% copper, 49% boric acid, and 2% tebuconazole. More recently, a copper azole preservative containing 96% copper and 4% tebuconazole has been manufactured. The copper in copper azole systems provides the primary fungicide and insecticide activity. The azole component protects against copper tolerant fungi, and thus acts as a co-biocide.

During the preservation process, proper handling and conditioning of the wood after treatment helps minimize leeching and potential environmental impacts for these preservatives. Amine keeps copper soluble in these treatment solutions. After preservative treatment, wood has to be thoroughly dried and suitably stabilized.

In the copper azole (CA–B) preservative, copper stabilization is very rapid occurring within 24 h at a retention of 1.7 kg m^{-3}. However, the stabilization process slows down to a large extent at higher retentions unless the wood is heated to enhance the stabilization [53].

With increasing demand for wood products, utilization of wood composites will increase, and these composite products also need to be protected with suitable wood preservatives. Thus, in the wood preservation industry, there is the need for superior alternative technologies to the traditional preservatives and pressure-treatment processes. In this instance, the development of effective and economical 3rd generation organic preservatives for wood used in areas with high or severe decay and deterioration hazards, will be interesting. The wood preservation industry needs to develop high-value products with desirable and dependable properties that have a high economic return sufficient to encourage companies to undertake the long-term and expensive research necessary to create azole-based preservatives for the future.

11. Challenges of azoles in wood preservation

There are known risks to aquatic communities associated with the use of azole-based wood preservatives. For instance, it has been established that micronized copper azole represents a source of harm to marine benthic communities comparable to that from copper salts, such as copper sulfate. There is therefore a need for better understanding of benthic community interactions when exposed to nanomaterial stress [55].

The increased use of copper azole as wood preservative for residential construction has exposed the preservative as causing corrosion to fasteners. There is limited evidence on the effects of these preservatives on the corrosion rate of the fasteners. However, Simpson Strong Tie has a technical bulletin publication which indicates that both ACQ and copper azole are roughly twice as corrosive as chromate copper arsenate (CCA) and gives recommendations on fastener types for a given environment and preservative [56].

Recently, however, the durability of fasteners in preservative-treated wood has been a key concern. Changes in legislation and certification in some countries have restricted the use of chromate copper arsenate (CCA), which used to be the most extensively used waterborne wood preservative [57]. Ensuing these changes, several different wood preservatives have come to the market, some of which are much more corrosive than CCA [58].

Prospective health effects of exposure to copper azole preservative are shown in **Table 2**. Tebuconazole is slightly persistent in the environment, and it is not mobile. Also, light intensely increases the degradation progression. Tebuconazole degradation is approximately 20% in water according to the Organization for Economic Co-operation and Development's Test Guideline 301C. Its half-life in soil is around 100 days. Tebuconazole is considered moderately toxic to aquatic organisms and has a slight potential to bioconcentrate, but it is rapidly eliminated from fish [59].

12. Opportunities for utilizing azoles in wood preservatives

Both old and new structures are susceptible to mold infestation in the absence of moisture. Treatment of wood products with nontoxic, nonvolatile fungicides adds a level of protection against mold infestation. However, these preservatives have corrosion problems. Use of azole-based fungicides to protect wood from indoor mold infestations is one strategy to address this problem. Although a lot of recent

(Wolman® NB)		**Possible health effects**	
Exposure category (Route of Entry)	**Type of exposure**	**Short-term exposure**	**Long-term exposure**
Estimated daily intake from various sources (air, water, food) with limited to no heath effect[a]			
Copper (an essential element)	2.47 mg/day		
Eye contact[a,b]	Direct contact	CA-B concentrate is corrosive	Ulceration, may cause irreversible damage
		Will cause irritation, pain and reddening	
Skin contact[a,b]	Significant skin contact with concentrates	Short term (up to 1 hour)	Long term
		Mild to moderate skin irritation, inflammation, reddening	Severe irritation, ulceration, chemical burns
ACGIH threshold limit value-time weighted averages (TWAs)[c]	Ethanolamine: 8 mg/m^3 air 3 ppm		
Exposure to airbome contaminant or dust inhalation[a,b]	Inhalation of mists, droplets or dust of concentrates	May cause upper respiratory tract irritation	Moderate to severe irritations of mucous membrane, nose, throat and lungs
		Moderate irritation of nose, throat and lungs	
ACGIH threshold limit value-time weighted averages (TWAs)[c]	Copper (dusts and mists): 1.0 mg Cu/ m^3 air	Irritation of eyes	Irritation of eyes

[a]*International Labour Organization ICSC Card database, http://www.ilo.org/dyn/icsc/showcard.home*
[b]*Agency for Toxic Substances and Disease Registry (ATSDR) http://www.atsdr.cdc.gov/substances/index.asp*
[c]*American Conference of Governmental Industrial Hygienists (ACGIH): http://www.acgih.org/tlv/*

Table 2.
Prospective health effects of exposure to copper azole preservative [59].

research has been conducted in this area, no attempt has been made to summarize all the recent advances, and confusion exists about the corrosiveness of alternatives to CCA and proper materials selection for use in treated wood. Thus, opportunities exist in searching for appropriate materials for the requisite preservatives.

Copper azole is a major copper-based wood preservative that has come into wide use in both developed and developing countries following restraints on CCA. The use of copper azole and other preservatives are directed by national and international specifications, which give the requirement for the volume of preservative application for a specific wood end-use. In terms of chemical composition, copper azole is similar to ACQ. The difference between them, however, is the dissolved copper preservative which is augmented by an azole co-biocide like organic triazoles such as tebuconazole or propioconazole, in the copper azole preservative. These preservatives are also used in food crops protection, instead of the quaternary biocide which is used in ACQ [60]. The azole co-biocide produces a copper azole compound that is effective at lower retentions than required for equivalent ACQ performance.

Wood treated with copper azole is marketed widely across many international markets. The AWPA standard retention for CA-B is 0.10 lb/ft^3 for above ground applications and 0.21 lb/ft^3 for ground contact applications. Copper azole type C

has been presented under the Wolmanized and Preserve brands. The AWPA standard retention for CA-C is 0.06 lb/ft^3 for above ground applications and 0.15 lb/ft^3 for ground contact applications. Opportunities exist for local standardization of these copper-azole preservatives as well as expanded local markets. Also, research question on how azoles contribute to the leaching of copper in treated wood is significant.

13. Environmental impact of azoles utilization

Azoles are widely used and efficient fungicides commonly employed to treat and prevent fungal diseases in humans and animals, as well as in food production, horticulture and wood industry. Residues of azoles in nature are regarded as environmental toxins and suggested to have general endocrine-disrupting properties. It has been suggested that triazole resistance has evolved in the environment and could be driven by the selective pressure of azole fungicides [61].

A significant challenge facing treated wood products is the lack of an effective strategy for handling treated wood that has been removed from service [61]. Until recently, the fixation processes of the amine wood preservatives were poorly understood, but ongoing research in North American university laboratories is beginning to expand the knowledge base considerably [62].

Some research works have shown that copper azole-treated wood can be chipped or flaked and recycled to form durable panel products or wood composites. However, this type of recycling has not gained significant commercial acceptance because of concerns with processing the treated wood. Recycling of the treated wood releases the preservatives into the panel fabrication process, which leeches into the environment, with consequent adverse impacts [63].

The widespread use of azoles in biomass preservation can affect the environment and the phytopathogens therein, with concomitant medical implications [64]. Accordingly, with azole treatment, fungi causing important human mycoses may develop azole-resistance [64, 65]. Azole as fungicide is very significant, as some human diseases are caused by fungi such as Aspergillus, Histoplasma, Coccidioides and Cryptococcus that survive in different environments [65].

14. Conclusion

Azole-based solar cells, fuel cells, and wood preservatives are of critical importance in energy applications and wood treatment, respectively. Multiple benefits are accrued from exploring this type of research in organic chemistry. Firstly, it will help in unraveling the intrinsic chemical behavior of azoles and their interactions with other molecules. Secondly, it will significantly help in the advancement of novel synthetic methods. Thirdly, using spectral methods for the characterization of a set of compounds could create benchmarks for similar molecules. In the next step, structure–activity relationships of azoles applications in energy and wood preservation will enhance their utilization. Finally, biological evaluation of the synthesized azole compounds may explore lead-compounds for further structural fine-tuning. Among the broad array of organic compounds, those incorporating one or more sulfur or nitrogen atoms like azoles are of great significance because of their unique properties imparted by these elements.

There are four main determinants as to how well an OSC will perform in a device: oxidative and thermal stability, properly aligned energy levels, good thin-film morphological characteristics, and purity and defects. The more researchers

explore azole functions, the greater the possibility for OPV to demonstrate at last its enormous potential on the industrial scale.

Recommendations for additional steps to assess the risks and consequences of the environmental usage of azole derivatives are pertinent. With azoles applications in both solar cells and fuel cells, where electronic excitations and ions mobility properties respectively of the azoles are taken advantage of, a solar PV/fuel cell hybrid energy systems for stationary applications employing azoles, could be embarked upon, and preliminary energy and exergy efficiency analyses performed for the hybrid energy system. Such a system, built on different scientific principles, can convert solar energy and chemical energy of fuel to electrical energy simultaneously within the same system.

For azole-based fuel cells and solar cells to achieve widespread production and adoption in energy applications, especially in developing countries, it is necessary to decrease their cost of production. Also, an increase in research output in the area and improvement in the range of environmental conditions under which they effectively operate will ensure widespread production and adoption in energy applications.

A broad approach that combines preservative formulations, treatment efficiency, component interaction studies, and carefully designed strategies for azole-based wood preservative utilization is needed. This approach will increase preservative efficacy, corrosion resistance, and reduce the risk of environmental pollution, and prevent azole-resistant infections. Improved research work, including azole-based preservative optimization and modeling, is a significant key to a better understanding of the magnitude of this emerging approach.

Author details

Nana Derkyi
University of Energy and Natural Resources, Sunyani, Ghana

*Address all correspondence to: nana.derkyi@uenr.edu.gh

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